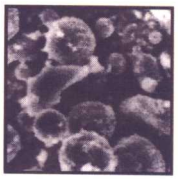

Innovative Processing and Synthesis of Ceramics, Glasses, and Composites III

Edited by
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Proceedings of the Innovative Processing and Synthesis of Ceramics symposium, held at the 101st Annual Meeting of The American Ceramic Society, Indianapolis, Indiana, April 25–28, 1999.

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COVER PHOTO: "SEM micrograph for as-sprayed powders after post-heating treatment" is courtesy of F. Boey, L.H. Cao, L. Fu and K.A. Khor, and appears as figure 8 in their paper "Characterization of AlN/Al_2O_3 Composite Powders Prepared by Thermal Plasma Method," which begins on page 81.

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Preface

This volume contains papers presented at a symposium on Innovative Processing and Synthesis of Ceramics, Glasses, and Composites held during the 101st Annual Meeting and Exposition of The American Ceramic Society in Indianapolis, April 25–28, 1999. This symposium provided an international forum for scientists and engineers to discuss all aspects of processing and synthesis of ceramics, glasses, and composites. A total of 167 papers, including invited talks, oral presentations, and posters, was presented from 22 countries (the United States, Belgium, Canada, France, Germany, India, Israel, Italy, Japan, Mexico, the Netherlands, the People's Republic of China, Republic of Korea, Singapore, Spain, Sweden, Switzerland, Taiwan, Turkey, Ukraine, Venezuela, and Yugoslavia). The speakers represented universities, industry, and research laboratories.

This volume contains 56 invited and contributed papers, all peer-reviewed according to American Ceramic Society procedures. The latest developments in processing and characterization are covered: combustion synthesis, powder processing, microwave/plasma/laser processing, preceramic polymer processing, rheological properties, sol-gel processing, reaction-forming/bonding, shock compaction, freeze drying, centrifugal casting, nanotechnology, microprocessing, rapid prototyping and laminated object manufacturing, fused shape deposition and mold shape deposition manufacturing, electrophoretic deposition, joining methods, processing-microstructure-property relationships, characterization, intermetallics, thin films and composites. All of the most important aspects necessary for understanding and further developing ceramic processing and characterization are discussed.

The organizers are grateful to all participants and session chairs for their time and effort, to authors for their timely submissions and revisions of the manuscripts, and to reviewers for their valuable comments and suggestions; without the contributions of all involved, this volume would not have been possible. Financial support from The American Ceramic Society is gratefully acknowledged. Thanks are due to the staff of the meetings and publications departments of The American Ceramic Society for their tireless efforts. Especially, we greatly appreciate the helpful assistance and cooperation of Sarah Godby throughout the production process of this volume.

We hope that this volume will serve as a useful reference for professionals working in the field of synthesis and processing of ceramics, glasses, and composites.

J.P. Singh
Narottam P. Bansal
Koichi Niihara

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COMBUSTION SYNTHESIS OF CALCIUM PHOSPHATE POWDERS

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ABSTRACT

Calcium phosphate bioceramic powders closely resembling those found 'in vivo' in human body (hydroxyapatite and tri-calcium phosphate) have been synthesized by using synthetic body fluid solutions via the combustion synthesis (CS) method. Powder characterization was performed by XRD, ICP-AES, FTIR and SEM.

INTRODUCTION

Calcium hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$), the main inorganic matrix component of bones, is a member of "apatite" family. Biological apatites, which comprise the bioinert mineral phases of calcified tissues (enamel, dentin, and bone), differ from pure HA in stoichiometry, composition and crystallinity and in other physical and mechanical properties [1]. Minor elements, such as, Na^+, Mg^{2+}, K^+, acid phosphate $(HPO_4)^{2-}$, Cl^-, and F^-, and some trace elements (e.g., Sr^{2+}, Pb^{2+}, Ba^{2+}, Zn^{2+}, Fe^{2+}, etc.) are associated with biological apatites and may be seen as substituents in the apatite structure. On the other hand, the presence of resorbable calcium phosphate ceramics in human bones (such as, tricalcium phosphate, TCP: $Ca_3(PO_4)_2$) is mainly for the establishment of a mineralized framework for bone remodeling.

HA or TCP powders have generally been synthesized from aqueous solutions for use in bioceramic applications. It is known [2] that calcium hydroxyapatite is the least soluble and the most stable calcium phosphate phase in aqueous solutions at pH values higher than 4.2. However, HA has been preferred to be synthesized in neutral or highly alkaline media [3-10] to insure the thermal stability of the formed phase after high-temperature (1100°-1300°C) sintering. Synthesis of HA in neutral [5] or slightly acidic media [8] is known to be a more complicated and difficult task. The synthesis of bi-phasic mixtures of the phases of HA and TCP has also been studied by aqueous coprecipitation [11].

The synthetic body fluid (SBF) prepared in accord with the chemical analysis of human body fluids, having the ion concentrations nearly equal to the inorganic components of human blood plasma, was first used by Kokubo and his co-workers [12-14], to prove the similarity between *in vitro* and *in vivo* behaviors of certain glass-ceramic compositions. Combustion synthesis (CS) is not a new technique to be used in the field of materials synthesis. It has first been used by Kingsley and Patil [15] for the manufacture of high-purity α-alumina powders. The same researchers have also

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successfully used this method of materials synthesis in preparing several compositions in the ZrO_2-Al_2O_3 binary system [16]. The combustion being instantaneous and energy-saving have attracted much interest and been successfully utilized in the synthesis of $LaCrO_3$ [17], $Ba_2YCu_4O_8$ [18] and Y-Ba-Cu-O phases [19]. Recently, combustion methods using "glycine" as the fuel [20], and "urea" as the fuel [21, 22] have been reported for the preparation of Ca-doped $LaCrO_3$, pure $LaAlO_3$ and the binary phases of the CaO-Al_2O_3 system, respectively. A similar combustion technique was also demonstrated for the synthesis of YAG:Cr and Y_2O_3:Eu [23], and of YAG:Nd and YIG:Nd [24] powders using both of the above-mentioned fuels.

The purpose of this study was to prepare phase pure HA and bi-phasic HA-TCP bioceramic powders by using the technique of combustion synthesis in synthetic body fluid solutions containing dissolved calcium nitrate tetrahydrate and di-ammonium hydrogen phosphate salts, and to investigate their high temperature (600°-1150°C) calcination behavior in a stagnant air atmosphere.

EXPERIMENTAL PROCEDURE

The details of preparation of the synthetic body fluid (SBF) solutions used in this study were given in Table I.

Table I Preparation of Synthetic Body Fluids

Order	Reagent	Amount (gpl)	Ion	Concentration (mM)
1	NaCl	6.429	Na^+	142
2	$NaHCO_3$	2.520	Cl^-	125
3	KCl	0.373	HCO_3^-	30
4	$Na_2HPO_4.2H_2O$	0.178	K^+	5
5	$MgCl_2.6H_2O$	0.305	Mg^{2+}	1.5
6	$CaCl_2.2H_2O$	0.368	Ca^{2+}	2.5
7	$ZnCl_2$	0.136	HPO_4^{2-}	1
8	$CuSO_4.5H_2O$	0.125	Cu^{2+}	0.5
9	$FeC_6H_5O_7.3H_2O$	0.897	Fe^{2+}	3
10	$(CH_2OH)_3CNH_2$	6.057	Zn^{2+}	1
			SO_4^{2-}	0.5

The Merck-purity chemicals listed in the second column of this table were first added (by the amounts given in the third column) into 700 mL of boiled de-ionized water in the order given in the first column. The solution was heated to 37°C and then completed to 1 L by adding aliquots of a total of 25 mL of 1 M HCl (for pH adjustment to 7.4) together with the required amount of de-ionized water. After adjusting the volume to 1 L, the nominal ion concentrations in the prepared SBF solutions were as given in the fourth and fifth columns of Table I (with the only exception of Cl^-, which is going to be higher than the value given there due to the

titration with HCl solution). Human plasma is known to contain small amounts of elements like Fe, Cu, and Zn [25].

The solutions used during the combustion synthesis were prepared as shown in Table II in seven groups of experiments (each repeated thrice for reproducibility). A 50 mL portion of the above SBF solution was placed in a clean Pyrex beaker of 250 mL capacity. $Ca(NO_3)_2.4H_2O$ and $(NH_4)_2HPO_4$ salts, of the amounts given in Table II, were respectively added into this solution.

Table II Experimental compositions studied by CS

Run	$Ca(NO_3)_2.4H_2O$ (gram)	$(NH_4)_2HPO_4$ (gram)	Ca / P (molar)
1	1.457	0.465	1.75
2	1.457	0.479	1.70
3	1.457	0.494	1.65
4	1.457	0.509	1.60
5	1.457	0.526	1.55
6	1.457	0.543	1.50
7	1.457	0.562	1.45

Thus formed opaque solution was then converted into a clear one, by adding 0.5 mL of concentrated nitric acid while stirring on a stir-plate at room temperature. 3 grams of urea was finally added into the clear solution, and following 2 minutes of stirring at room temperature, the Pyrex beaker was directly placed into an electrically-heated box furnace maintained at 505 ± 10°C. Initially the mixture boils and undergoes dehydration followed by decomposition, with swelling and frothing, resulting in a foam which ruptures with a flame and glows to incandescence [16]. The entire combustion process was complete in less than 15 minutes [22]. The product of combustion was a voluminuous, beige in color, foamy, crystalline and crisp calcium phosphate precursor. The precursors were lightly ground in an agate mortar into a fine powder and then calcined on α-alumina plates, in a stagnant air atmosphere, over the temperature range of 600° to 1150°C, for 17 hours.

Powder X-ray diffraction spectra were obtained from the as is and calcined samples for phase characterization purposes. A Rigaku (Tokyo, Japan) DMax/B powder diffractometer was used with CuK_{α_1} radiation at the step size of 0.02° and a preset time of 5 seconds. The FTIR spectra of the powder samples were collected by a Nicolet (USA) DX-510 spectrometer. Dried (at 90°C) powder samples were mixed in an agate mortar with 3 wt% KBr prior to pellet formation. Particle size and morphology of the powders were investigated from the photomicrographs taken with a JEOL (Tokyo, Japan)/JSM6400 scanning electron microscope. The samples were, first, sputter-coated with an approximately 25 nm-thick layer of Au-Pd alloy. Inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin Elmer,

Model: Plasma-1000, UK) was used for the accurate chemical analysis of elements present in the produced calcium phosphate powders.

RESULTS AND DISCUSSION

Nitrate solutions usually decompose at temperatures <700°C with the evolution of the gases of nitrous oxides, such as NO_2, NO, and N_2O_5 [19]. Urea is also known [19, 22] to decompose into biuret (H_2N-CO-NH-CO-NH_2, i.e., $C_2H_5N_3O_2$), cyanuric acid (HCNO), ammonia (NH_3) when it is heated to about 200°C. Biuret itself then decomposes when heated at temperatures >300°C. Therefore, in an aqueous mixture of a metal nitrate and urea, the decomposition products are expected to consist of nitrous oxides, NH_3, and HCNO. This gaseous mixture will spontaneously ignite when the ambient temperature is about 500°C [22]. This ignition is believed to instantaneously increase the local temperature of the dried foam to about 1300°C [19], which, in a sense, is similar to the case of flash pyrolysis.

Figure 1 shows the XRD spectra of the combustion-synthesized calcium phosphate compositions listed in Table 2. The samples of this figure were all calcined in air at 1150°C for 17 h, following the CS. The variation in the nominal Ca/P (molar) ratio in the starting CS solutions was found to provide a powerful control in the final phase assemblage (in terms of HA and TCP distribution) of the 1150°C-calcined powders. Single-phase HA powders were only obtained for the Ca/P ratio (in the initial solutions) in excess of 1.70. Samples prepared from solutions with Ca/P < 1.70 all yielded bi-phasic mixtures of HA-TCP. In other words, the amount of TCP in the two phase mixtures increased with decreasing Ca/P ratio as follows; 5% TCP at 1.70, 10% TCP at 1.65, 15% TCP at 1.60, 35% TCP at 1.55, 80% TCP at 1.50, and 95% TCP at 1.45. Phase assemblage in these samples consisted of a mixture of both α- (high-T) and β- (low-T) polymorphs of tri-calcium phosphate. The powder synthesis method presented here is regarded as a quick way of producing the bi-phasic mixtures of HA-TCP, as well as for pure HA.

Figure 2 shows the XRD spectra of the combustion-synthesized powder samples by using an initial (solution) Ca/P ratio of 1.75, after being heated at different, consecutively increasing temperatures. The "as is" powders obtained immediately following the CS process were found to be crystalline, and they basically consisted of the phases of $Ca_8H_2(PO_4)_6.5H_2O$ (ICDD PDF 26-1056), $Ca(OH)_2$ (PDF 4-733) and CaO (PDF 4-777). After heating (15°C/min heating and 5°C/min cooling) these powders in a stagnant air atmosphere at 600°C for 17 h, the above phase assemblage was almost retained. Calcination of the same powders at 800° and 1000°C caused the initial formation of HA phase (ICDD PDF 9-432), and the powders heated at 1150°C were found to consist of single-phase calcium hydroxyapatite. The lattice parameters of the 1150°C-calcined HA samples were measured to be a = 9.431 and c = 6.884 Å. These values were in good agreement with those reported [26] for bone apatites.

The results of the ICP-AES analysis performed on the 1150°C-calcined, combustion-synthesized HA powder samples were given in Table III. The samples were first dissolved in HNO_3 and the ICP analysis were carried out on these solutions.

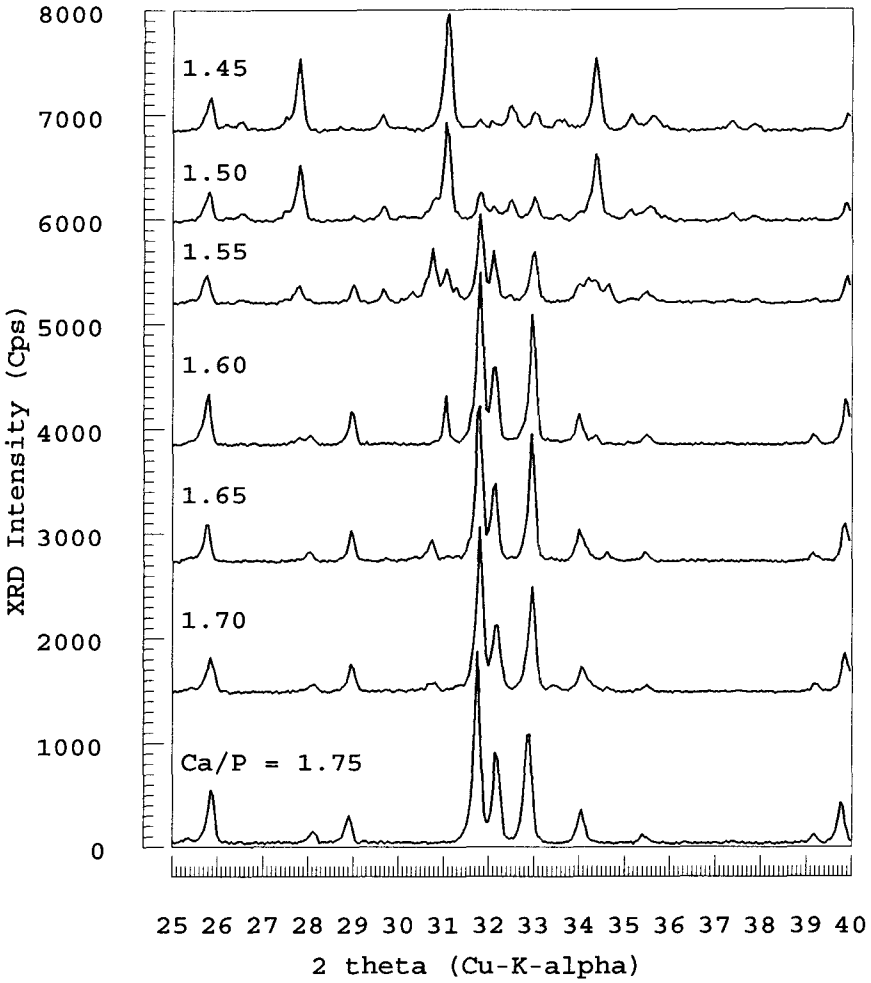

Fig. 1 XRD spectra of combustion-synthesized calcium phosphate compositions given in Table 2 (1150°C, air, 17 h)